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Spectral hole burning of Eu^{2+} in selectively doped CaF_2:Eu/CdF_2 superlattices

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Introduction

It has been recently shown [1] that Eu^{2+} $4f^6 5d \rightarrow 4f^7$ photoluminescence (PL) quenching in CdF_2/CaF_2:Eu superlattices (SL) grown on Si(111) [2] is due to the tunneling of electrons from $4f^6 5d$ excited state of Eu^{2+} to the conduction band of the neighboring CdF_2 layer. The probability of tunneling for an electron from an Eu^{2+} ion residing at CaF_2/CdF_2 interface at distance z, through a barrier ΔE is given by eq. (1):

$$W_t = \frac{2\Delta E}{\pi\hbar}\exp\left(-\frac{z}{z_0}\right), \qquad z_0 = \sqrt{\frac{\hbar}{8m\Delta E}} \tag{1}$$

where $\Delta E \sim 0.3$ eV [1] is the thermal ionization energy of the Eu^{2+} $4f^6 5d$ excited state in CaF_2 and $z_0 \sim 0.2$ nm (supposing $m = m_0$). Using eq. (1) one can estimate that at a distance $z_{\rm crit} \sim 3.2$ nm (10 monolayers (ML) of fluoride) the probability of tunneling W_t equals the probability of radiative recombination $W_R \sim 2 \times 10^6$ s^{-1} [3].

It is known that hole burning spectroscopy is very usefull for investigating dynamic processes in the excited state. However most of such experiments have been carried out in bulk crystalls. In this paper we investigate the burning of spectral holes in the Eu^{2+} zero-phonon line in doped SLs, first observed in [4]. Two mechanisms of hole burning are considered: the tunneling-assisted and two-step photoionization processes. To separate these, both homogeniously and selectively doped SLs are studied. It is shown that relative contribution of the two processes depends strongly on the spatial distribution of Eu^{2+} ions in the fluorite layer.

Experiments and discussion

For our studies of hole burning three SLs were grown as described in [2]:

SL #24	[CdF_2 60 ML |	|	CaF_2 : Eu 60 ML |	]×8 |	Si(111)
SL #60	[CdF_2 60 ML |	CaF_2 10 ML |	CaF_2 : Eu 40 ML |	CaF_2 10 ML]×8 |	Si(111)
SL #95	[CdF_2 20 ML |	|	CaF_2 : Eu 20 ML |	]×8 |	Si(111)

In structures #24 and #95, CaF_2 layers were uniformly doped with Eu^{2+}. In sample #60, a spacer of pure CaF_2 was introduced at each CaF_2/CdF_2 interface, so that only central part of each CaF_2 layer was doped. The concentration of Eu^{2+} ions was 2×10^{19} cm^{-3} (~ 0.1 mol.%). Band energy level diagrams of these SLs are presented in Fig. 1.

From eq. (1) it is seen that W_t becomes considerably less than W_R for ions located more than 10 ML from the interface. Taking into consideration the high excitation power (8 ns laser pulses each carrying 0.1 mJ focused in a spot 1mm in diameter) and the large cross-section of the $4f^6 5d \rightarrow CaF_2$ conduction band transition ($\sigma_{\rm ex} \sim 10^{-19}$ cm^{-2}

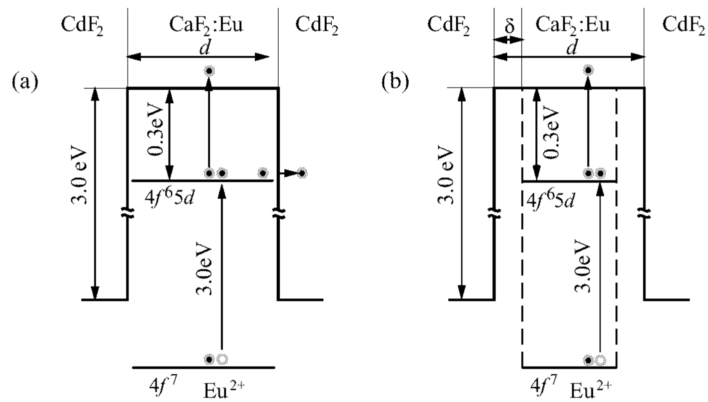

Fig 1. Energy levels of Eu^{2+} in CdF_2/CaF_2:Eu superlattice (a) uniformly doped SLs #24 and #95, (b) selectively doped SL #60.

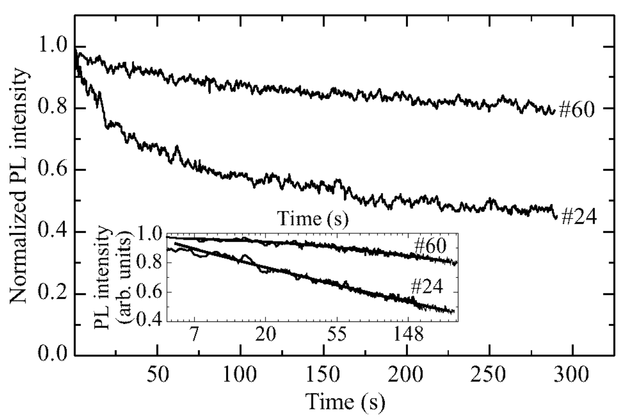

Fig 2. PL behavior in SLs #60 and #24 under continuos resonant excitation of the $4f^7 \to 4f^6 5d$ transition with a pulsed laser ($\lambda = 413.6$ nm) at $T = 2$ K. The inset represents the same dependences with a logarithmic scale.

if excited with $\lambda = 413$ nm photons), we suppose that a two-step photoionization process takes place with a probability for the second step of $W_{PI} \sim 10^5\ s^{-1}$.

Both tunneling to the CdF_2 layers and two-step ionization with further thermalization of electrons from the CaF_2 conduction band to the CdF_2 wells will decrease the number of Eu ions in the divalent state. This will result in quenching of Eu^{2+} PL (measured from its vibronic sideband luminescence) under resonant excitation of the f–d transition. Fig. 2 shows that under the same excitation conditions the quenching effect is considerably stronger in homogeneously doped sample #24 than in the selectively doped #60. The logarithmic behavior of the quenching for sample #24 (inset on Fig. 2) provides convincing evidence for the dominant role of the tunneling-assisted photoionization [1]. For sample #60, with no Eu^{2+} ions residing near the interface, the tunneling process is less effective while the rate of two-step photoionization is the same as that in sample #24.

Excitation of the f–d transition was carried out with $\lambda = 413$ nm laser radiation having a spectral width of 0.2 cm^{-1} (6 GHz) which is considerably less than the zero-

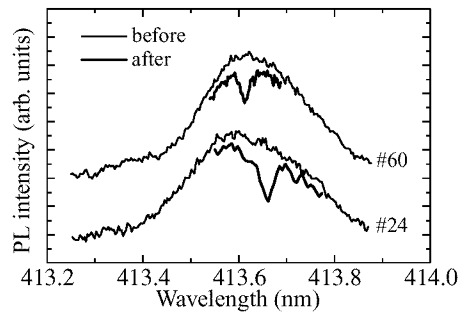

Fig. 3. PL excitation spectra of $4f^7 \to 4f^6 5d$ transition in SLs #24 and #60 before and after the hole burning. Laser irradiation is 5 times weaker than used for the hole burning. T = 2 K.

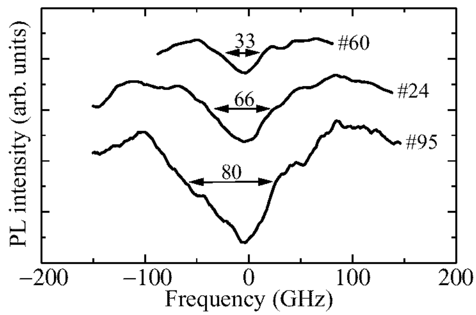

Fig. 4. The shape of spectral holes in the excitation spectra in SLs #60, #24, #90 after burning for 400 s.

phonon PL line width of Eu^{2+} ($\sim$ 18 cm^{-1} in the SLs studied). For this reason the PL quenching shown in Fig. 2 results in the burning of a hole in the Eu^{2+} zero-phonon line (Fig. 3). Fig. 3 shows practically the same band shape for both SLs. The positions of their maxima demonstrate the coherentness of the SLs to their substrates while their relatively small width is evidence for the high degree of structural perfection of the CaF_2 layers [5]. The width of spectral holes varies for different SLs (Fig. 4): from 33 GHz in sample #60 to $\sim$ 80 GHz in #95 and greatly exceeds the value of 0.5 GHz obtained for persistent hole burning in bulk CaF_2:Eu [6].

To explain the broadening of the spectral holes, one must take into consideration specific features of SLs arising from the presence of the CdF_2 layers. Because the bottom of conduction band lies at $\sim$ 2.6 eV below the $4f^6 5d$ level of Eu^{2+} (Fig. 1), the CdF_2 layers act as traps for both tunneling electrons and for electrons thermalized after a two-step photoionization process. The electron transfer results in the formation of a positively charged layer near the interface consisting of trivalent Eu ions and a negative charge of quasi-free electrons accumulated in CdF_2.

Narrow line laser radiation excites only those Eu^{2+} ions whose f–d transition energy is exactly equal to that of the photons. However after a fraction of these ions become ionized the charge separation occurs near the interface inducing an internal electric field. A Stark-shift of the Eu^{2+} f–d transition energy [7] may result in involvment of initially non-resonant Eu ions into the ionization process. To estimate the role of the Stark shift it seems reasonable to use the value of internal electric field E_{int} at the interface. This can be obtained after calculating the number of ionized Eu ions obtained by comparing the area of the spectral hole with the area of the whole zero-phonon band (Fig. 3). Considering the interface area as a plane capacitor we obtain $E_{int} = 10^6$ V/cm. Using the value of $5 \times 10^{-13}\,cm^{-1}(V/cm)^{-2}$ for the quadratic Stark shift of the $f-d$ transition energy of the centrosymmetric Eu^{2+} cubic sites in CaF_2 [8], we estimate the shift in our SL to be about 0.5 cm^{-1} ($\sim$ 15 GHz).

This shift allows us to explain 30 GHz wide spectral hole in sample #60 (Fig. 4). However, in order to explain the wider spectral hole widths in samples #24 and #95 (66 GHz and 80 GHz respectively) other processes must be considered. The remarkable feature of SLs #24 and #95 is that the ionization of Eu is mainly ascribed to tunneling which is known to be considerable in a 20 ML wide layer at each interface. The larger fraction of Eu ions residing in those layers, the shorter will be the time for the PL intensity to decrease and come into saturation. Here we assume that there are two processes of Eu ionization taking place with different rates: fast tunneling from the interface region and two-step photoionization which is noticeably slower.

Excitation of those Eu^{2+} ions whose zero-phonon f–d transition is resonant with the laser dominates. In addition, some less probable phonon assisted transitions may excite Eu ions whose zero-phonon line is not resonant with the laser. In spite of the relatively small rate, those transitions may result in some broadening due to additional hole burning on the both sides of the main spectral hole, provided we carry out the hole burning long enough to saturate the hole burning in the zero- phonon transitions. Then the slow phonon-assisted processes may become noticeable. The situation is similar to that which occurs for light detection by a photographic plate.

The fraction of Eu ions located in the vicinity of the interface increases considerably in the sequence of SLs #60, #24 and #95 leading to a corresponding reduction in the time for saturation of the ionization of the hole in the zero-phonon line. In this same sequence, the side band features become more pronounced as can be seen from the width of each spectral hole (Fig. 4).

Conclusions

It is demonstrated that persistent hole burning in the zero-phonon line of Eu^{2+} in SLs of CaF_2:Eu/CdF_2 with uniformly doped CaF_2 layers is mainly due to tunneling of electrons from the $4f^6 5d$ excited state of Eu^{2+} to the conduction band of adjacent CdF_2 layer. However in selectively doped SLs, the two-step photoionization process dominates in the formation of spectral holes. Two mechanisms of spectral hole broadening were discussed. These are the Stark-shifting of the Eu^{2+} f–d transition energy induced by internal electric field and phonon assisted transitions.

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